[JP,2001-164354,A]

Japanese (PDF) | File Wrapper Information

FULL CONTENTS CLAIM + DETAILED DESCRIPTION TECHNICAL FIELD PRIOR ART EFFECT OF THE INVENTION TECHNICAL PROBLEM MEANS EXAMPLE

[Translation done.]

CLAIM + DETAILED DESCRIPTION

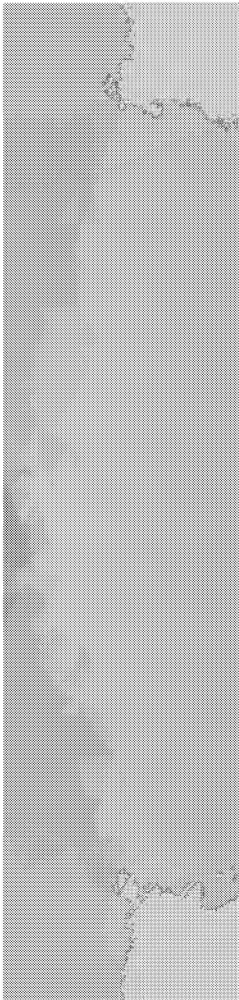
[Claim(s)]
[Claim 1] Inside material of a plasma treatment container characterized by covering the surface of a base material with 2OY3 sprayed coating.
[Claim 2] Inside material of a plasma treatment container according to claim 1 characterized by having a metallic film as an under coat under the Y2O3 sprayed coating formed as topcoat.
[Claim 3] Inside material of a plasma treatment container according to claim 2 characterized by having an intermediate layer between the metallic film formed as an under coat, and 2OY3 sprayed coating formed as topcoat.
[Claim 4] The metallic film of an under coat nickel and its alloy, W, and its alloy, Any one or more sorts of metals and the alloy which were chosen from Mo and its alloy, Ti, and its alloy are used, and it is 50-500. Inside material of a plasma treatment container according to claim 2 or 3 characterized by being the coat formed in mum thickness.
[Claim 5] an intermediate layer and Al2O3 -- or -- Inside material of a plasma treatment container according to claim 3 characterized by being formed with the mixed coat of Al2O3 and Y2O3.
[Claim 6] The intermediate layer who consists of a mixed coat of Al2O3 and Y2O3 is at the under coat side. Inside material of a plasma treatment container according to claim 5 characterized by being the layer in which the concentration of Al2O3 is high and, on the other hand, has inclination concentration with high concentration of Y2O3 by the topcoat side.
[Claim 7] 2OY3 sprayed coating is the inside material of a plasma treatment container given in Claim 1 - any 1 clause of five which are characterized by the porosity being 0.5 to 10% in the range which is 50-2000 micrometers of thickness.
[Claim 8] The manufacture method of the inside material of a plasma treatment container which covers Y2O3 with a spraying process and is characterized by forming 2OY3 sprayed coating on the surface of a base material.
[Claim 9] On the surface of a base material, apply any one or more sorts of surface treatment methods of a CVD method, the PVD method, or a spraying process, and as an under coat The manufacture method of the inside material of a plasma treatment container which covers the metal which consists of nickel, W, Mo or Ti, and those alloys, and is characterized by forming a compound layer by covering Y2O3 as topcoat on it.
[Claim 10] On the surface of a base material, any one or more sorts of surface treatment

[Translation done.]

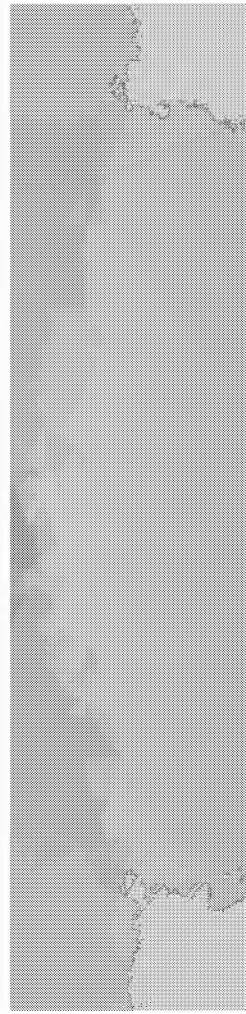
methods of a CVD method, the PVD method, or a spraying process are applied. Cover the metal which consists of nickel, W, Mo or Ti, and its alloy, and an under coat is formed. subsequently, the under coat top -- Al2O3 -- or -- The manufacture method of the inside material of a plasma treatment container characterized by covering the mixture of Al2O3 and Y2O3, forming an intermediate layer, covering Y2O3 and forming topcoat on the intermediate layer after that.

[Detailed Description of the Invention]
[0001]
[Field of the Invention] This invention relates to the inside material of a plasma treatment container which is excellent in plasma-proof erosion nature, and its manufacture method. Especially this invention is used by the plasma treatment in the plasma atmosphere of the raw gas containing a halogen element. For example, it is a proposal about technology applicable to DEPOSHIRUIDO, a baffle plate, a focus ring, an insulator ring, a shielding ring, a bellows cover, an electrode, etc. In addition, this invention is not restricted only to the field of semiconductor fabrication machines and equipment, and can be applied also to inside articles of a plasma treatment container, such as a liquid crystal device, again. The example of semiconductor fabrication machines and equipment mainly explains hereafter.
[0002]
[Description of the Prior Art] general -- manufacture processes, such as a semiconductor and a liquid crystal device, -- the inside of a treatment container -- a **** ghost like BF3 or NF3, and BCl3 Chlorides, such as SnCl4, and HBr like -- in order to use raw gas including a bromide, there was a problem that the inside material of a treatment container carried out corrosion consumption remarkably.
[0003] As the material currently used in the plasma treatment container of semiconductor fabrication machines and equipment, Sprayed coatings, such as metallic materials, such as aluminum and an aluminum alloy, an oxide film on anode of aluminum covered on the surface, or boron carbide, and Al2O3 Polymer coats, such as a sintered compact coat and also fluorine resin, such as Si3N4, and an epoxy resin, are known. If such material touches a strong corrosive halogen ion, chemical damage is received or receiving erosion damage by particles, such as SiO2 and Si3N4, and the ion excited by plasma is known.
[0004] In particular, in the process using a halogenated compound, in order to attain much more activation of a reaction, plasma is often used. However, a halogenated compound is dissociated under such a plasma service condition. at the same time it generates F of the corrosive shape of a strong atom, Cl, Br, I, etc. very much -- the inside of the environment -- SiO2 if impalpable powder-like solid matters, such as Si3N4, Si, and W, exist With chemical corrosion, the member used into the plasma treatment container will receive strongly an operation of erosion damages to both by particles. And the environment where plasma was excited is the phenomenon in which the gas which does not have corrosiveness like Ar gas is also ionized, and this collides to a solid side strongly. (ion bombardment) Since it generates, it is also known that the various members currently arranged in the above-mentioned container will receive still stronger damage.
[0005]
[Problem(s) to be Solved by the Invention] Like the semiconductor fabrication machines and equipment mentioned above, there were the following problems about the following conventional member used in the intense field of chemical corrosion or erosion damage.
(1) aluminum and an aluminum alloy are anodized and it has corrosion resistance. Al2O3 film (alumite) About the material made to generate, when plasma erosion is received in the atmosphere containing halogen gas, there is a problem of being short-life. Moreover, since it is the coat containing aluminum, the particle of AlF3 occurs and invites the poor product of the semiconductor to manufacture.
(2) the member surface -- the PVD method and a CVD method -- the [, such as Sc, Y, La, Ce, Yb, Eu, and Dy, / periodic table] -- precise coats, such as an oxide of 3a group element, carbide, a nitride, and a **** ghost, are formed, or there is technology which applies the single crystal of Y2O3 (JP,H10-4083,A) . However, a deposition rate is late inferior to productivity, and also this technology forms two or more coat members simultaneously. (compound coat)

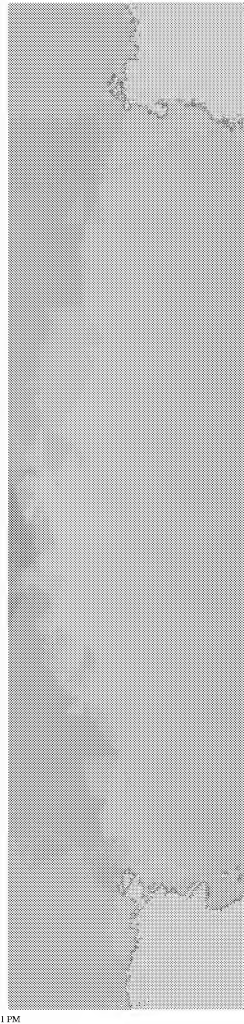
There is a fault that it cannot do.
[0006] Then, the purpose of this invention is in the place which proposes the surface treatment member with which the large plasma treatment container of resistance to the damage by the chemical corrosion by the environment where halogen gas is contained, and damage by plasma erosion etc. is presented, and its advantageous manufacture method.
[0007]
[Means for Solving the Problem] This invention is conquered by adoption of a solution means to summarize and describe below the problem and fault which the conventional technology is holding and which were mentioned above. That is, it is as follows when the composition of this invention is arranged.
[0008] (1) It is the covering member in which the layer which consists only of 2OY3 sprayed coating with a porosity [0.2 to 10% of] and a thickness of 50-2000 micrometers by a spraying process was formed on the surface of the base material.
[0009] (2) [in under the plasma development conditions in the atmosphere containing a halogenated compound] when environmental corrosiveness is strong On the surface of the base material, excelled in adhesion with 2OY3 sprayed coating by the spraying process preferably as an under coat. [the coat of one or more sorts of the metal and alloys chosen from nickel and its alloy, W and its alloy, Mo and its alloy, Ti, and its alloy] 50-500 It is the covering member which covered in the thickness of mum, and processed 2OY3 sprayed coating into 50-2000-micrometer thickness on the under coat, and formed the compound layer.
[0010] (3) To the surface of a base material, it is a metallic film. (preferably sprayed coating) After constructing as an under coat, On the under coat, it is an intermediate layer. Coat of Al2O3 (preferably sprayed coating) It is the covering member which formed and formed further the multilayer-like compound layer which forms 2OY3 sprayed coating by thermal spraying as topcoat on the intermediate layer.
[0011] (4) To the surface of a base material, it is a metallic film. (preferably sprayed coating) After constructing as an under coat, On the under coat, it is an intermediate layer. Coat of the mixture of Al2O3 and Y2O3 (preferably sprayed coating) It is the covering member which formed and formed further the multilayer-like compound layer which formed 2OY3 sprayed coating by the spraying process as topcoat on the intermediate layer.
[0012] (5) [2OY3 sprayed coating which constructed direct or the under coat, and the intermediate layer, and is formed upwards on the surface of a base material] [carry out / in the air / by using 2OY3 powder of 95% or more of purity / the plasma metal spray of this powder] It is the member which covered the sprayed coating obtained with the application of the thermal-spraying method which carried out the plasma metal spray under the decompressed atmosphere of the Ar gas which does not contain oxygen substantially, or was chosen from the high-velocity-flame-spraying method, the detonation-flame-spraying method, etc. The method of depending on low pressure plasma spraying of Ar gas is effective also for a corrosion resistance improvement especially.
[0013]
[Embodiment of the Invention] As a result of inquiring wholeheartedly about the technical problem which the conventional technology is holding and which was mentioned above according to research of inventors, the damage to the inside material of a plasma treatment container can consider damage by the chemical corrosion by halogen gas, and damage by plasma erosion. When this member was especially used in the atmosphere containing the halogen excited by plasma, it is important to just prevent the damage which considers plasma-proof erosion nature as a reason, then knowledge that it acts effectively also to chemical corrosion prevention was acquired. So, in this invention, it inquired about formation of the effective coat mainly to plasma-proof erosion nature. As the result, the member concerning this invention of upper ** was developed.
[0014] That is, fundamentally, this invention adopted as a means of the business solution was made to form the sprayed coating which consists only of Y2O3 in the base material surfaces, such as a metal, Ceramics Sub-Division, and a carbon material, by a spraying process. And when the corrosiveness of the environment where such a member is used is strong, while preparing the under coat of the metal in which the strong characteristics of halogen gas-proof corrosiveness are shown under said 2OY3 sprayed coating, it is in a pan. It is the method of also making the intermediate layer of Al2O3 or Y2O3 preparing and decoding. The composition of this this invention member is explained in detail hereafter.



[0015] (1) as a base material which is the construction target of the above-mentioned sprayed coating about a base material Various kinds of steel, aluminiums, and aluminium alloys containing stainless steel, Tungsten and a tungsten alloy, titanium and a titanium alloy, molybdenum, a molybdenum alloy, carbon, and oxide system, A non-oxide system ceramic sintered body or a carbonaceous material is suitable. In addition, since copper and a copper alloy are emitted by the corrosive action by plasma erosion or a halogenated compound and cause environmental pollution, they are not desirable. Therefore, when [of equipment] copper and a copper alloy need to be used constitutionally, Cr, nickel, etc. need to cover with means, such as electroplating, chemical plating, and vacuum evaporationo.
[0016] (2) [form / after formation of a coat on the above-mentioned base material surface carries out abrasive blasting of the base material / formation / membranes / about coat composition, / it carries out thermal spraying of Y2O3 directly, and] Or the method of PVD treatment, CVD-processing or thermal-spraying processing, and forming in the base material surface the coat which consists of a strong metallic material of halogen gas-proof corrosiveness as an under coat layer first, and using 2OY3 powder as topcoat, carrying out thermal spraying on the under coat, and using as a compound layer is desirable. In this case, said metal under coat (sprayed coating etc.) Thickness is 50-500. It carries out within the limits of mum. When an under coat layer is thinner than 50 micrometers, the operation effect as an under coat is weak, and on the other hand, it is 500. It is because an effect is saturated with the thickness exceeding mum, so there is no meaning of tylosis and it is not a best policy. As this metallic material for under coats, nickel and a nickel alloy, tungsten and a tungsten alloy, molybdenum and a molybdenum alloy, titanium, a titanium alloy, etc. are suitable.
[0017] [2OY3 sprayed coating used as topcoat] on the other hand construct directly on the base material surface -- moreover, carry out thermal spraying on said under coat, and make it a compound layer -- further -- as an intermediate layer Al2O3 the case where 2OAl2O3+Y3 coat is prepared -- be -- it is desirable to construct in thickness of 50-2000 micrometers anyway. This is because the effect saturates and is not more economical in a film than in 50 micrometers even if an effect is scarce and makes it thicker than 2000 micrometers on the other hand to prevention of damage by plasma erosion.
[0018] In addition, the porosity of 2OY3 sprayed coating of topcoat has 0.5 to 10% of good range. 0.5 It is because the coat below % is difficult to manufacture in a spraying process and inferior to corrosion resistance and plasma-proof erosion nature with the coat of the porosity of 10% or more.
[0019] (3) About 2OY3 sprayed coating of the member outermost superficial layer, the composition of this invention by which it is characterized most adopts Y2O3 as a material which shows plasma-proof erosion nature in the atmosphere which includes the outermost layer of a base material for halogen gas, and is in the place which carries out covering formation by making this into a thermal-spraying layer. That is, according to research of this invention, Y2O3, specific gravity was [4.84 and a fusing point] 2410 degrees C, and since chemical bonding strength with oxygen was strong, even if it received the plasma erosion operation in the atmosphere containing halogen gas, it turned out that the state where it was stabilized is maintained. However, this 2OY3 purity needs to use 95% or more of thing, and if impurities, such as Fe, Mg, Cr, aluminum, and nickel, Si, are contained as an oxide, since erosion-proof nature will fall, it is not desirable. The thing of 98% or more of purity is more desirable. In addition, intermediate layer who makes it form directly under this 2OY3 sprayed coating As for Al2O3, in a chemically stable top, there is little change under an air plasma metal spray or low-pressure-plasma-spraying environment, and it bears the operation which compensates the plasma-proof erosion nature of Y2O3.
[0020] (4) Let 2OY3 coat of outermost layer topcoat at least be a sprayed coating in formation this invention of a covering method a. sprayed coating. And it is the meaning which strengthens this coat further under this topcoat sprayed coating preferably, and it is desirable to make the whole coat composition into the following multilayer structures. That is, after constructing the under coat of a metallizing coat on the surface of a base material, an Al2O3 sprayed coating or inclination combination is started on it. The mixture sprayed coating of Al2O3 and Y2O3 is constructed as an intermediate layer, and 2OY3 sprayed coating is further formed as topcoat on it. The Reason nil why such coat composition is desirable is excellent in corrosion resistance and plasma-proof erosion nature as compared with a metallizing coat. It is



forming Al2O3 as an intermediate layer. It is because multilayer structure of the sprayed coating can be carried out, the penetration pore of a coat can be lessened and corrosion resistance and erosion-proof nature can be raised. And it is as an intermediate layer. Al2O3 demonstrates adhesion with both an under coat and good topcoat. In this meaning, it is more desirable to consider it as an intermediate layer and the layer of the mixture of Al2O3 and Y2O3, and it is the under coat side in this case. While making Al2O3 concentration high, in the topcoat side, it is desirable to consider it as the mixed layer concerning inclination combination to which 2OY3 concentration becomes high. Since such an intermediate layer's formation can be easily constructed if a spraying process is adopted, it can be called desirable embodiment that an intermediate layer is formed as a sprayed coating. In addition, the same range as 2OY3 sprayed coating of topcoat is suitable for an intermediate layer's thickness.
[0021] In this invention, it is a metal. In order to form the sprayed coating of Al2O3 and Y2O3, air plasma spraying or the plasma spraying in the inside of the atmosphere which does not contain oxygen substantially is suitable, but construction by high velocity flame spraying or a detonation-flame-spraying method is also possible.
[0022] b. Under coat by the CVD method and the PVD method, although a reduction deposit is carried out by hydrogen etc. and the steam of a necessary metal halogenated compound is oxidized with oxygen or an oxygen compound after that in an intermediate layer's formation CVD method By heating in the air, membranes are formed by making it change to an oxide film. On the other hand, by the PVD method, a sintered compact or powder is used as a raw material, an electron beam is glared and vaporized in this, and membranes are formed by depositing this on the base material surface. Formation of the coat generally according to a CVD method and the PVD method is a thin film. (for example, around 50 micrometers) It is suitable for construction.
[0023] (5) 2OY3 sprayed coating covered on the member surface which starts this invention about the service condition of the member concerning this invention is useful especially when using it under the plasma environment generated under the atmosphere containing a halogenated compound.
[0024] Of course, it compares with the atmosphere which is effective as for this invention and contains halogen especially in this case also to the plasma erosion operation under atmosphere, such as N2 which does not contain a halogen element or a halogenated compound, and H2. Since erosion damage is loose, the coat covering member concerning this invention demonstrates the performance stabilized over the long period of time.
[0025]
[Example] a work example 1 -- this work example -- specimen made from an aluminium (size: 5mm of 50mm[in width] x length [of 50mm] x thickness) using 2OY3 thermal spray material, after carrying out surface roughening of one side by abrasive blasting -- air plasma spraying, It is 50 - 200 hPa about an atmosphere pressure with Ar gas. By the controlled low-pressure-plasma-spraying method, it is thickness 300, respectively. mY2Omu3 sprayed coating was formed. Moreover, it is thickness 100 about the under coat of a nickel-20% aluminum alloy by air plasma spraying to one side of the specimen made from an aluminium. After constructing to mum thickness, said Y2O3 are used as topcoat, and it is 300. What was covered to mum thickness was produced. Then, the porosity of 2OY3 sprayed coating currently formed in these specimen surfaces, bond strength, and a spalling test (after heating in the electric furnace currently maintained by 500 degrees C for 20 minutes, operation of air cooling is made into 1 cycle out of a furnace, and it is 10 cycle ******** examination) It carried out. In addition, what was constructed at conditions with the same said of the sprayed coating of Al2O3 as a comparative example and the same process was offered as a sample.
[0026] Table 1 summarizes the test result at this time. The coat which suits this invention is what covered 2OY3 coat directly on the surface of the specimen. (No.1, 3) What began, gave the under coat upwards and formed 2OY3 coat (No.2, 4) Even if all the included coats compare good adhesion and thermal shock resistance with an example and an Al2O3 coat It is completely equal. Since especially 2OY3 coat formed by the low-pressure-plasma-spraying method has little porosity as compared with the coat of an air spraying process, it can also expect good corrosion resistance.
[0027]
[Table 1]



No.	溶射法	皮膜の構成		気孔率 (%)	密着強さ (MPa)	熱衝撃試験 外観目視	備考
		アンダーコート	トップコート				
1	大気プラズマ	なし	Y_2O_3	5 ～ 9	35 ～ 38	剥離なし	実施例
2		Ni－20Al	Y_2O_3	6 ～ 8	38 ～ 41	剥離なし	
3	減圧プラズマ	なし	Y_2O_3	0.2～ 3	40 ～ 41	剥離なし	
4		Ni－20Al	Y_2O_3	0.3～ 4	40 ～ 44	剥離なし	
5	大気プラズマ	なし	Al_2O_3	8 ～12	38 ～ 42	剥離なし	比較例
6		Ni－20Al	Al_2O_3	9 ～12	35 ～ 44	剥離なし	
7	減圧プラズマ	なし	Al_2O_3	0.5～ 5	38 ～ 44	剥離なし	
8		Ni－20Al	Al_2O_3	0.6～ 7	39 ～ 43	剥離なし	

（備考）
(1) 皮膜厚さ：アンダーコート 100μm、トップコート 300μm
(2) 密着強さは JIS H8666セラミック溶射皮膜試験方法規定の密着強さ試験法による。
(3) 熱衝撃試験： 500℃×20min →室温（空冷） 繰り返し10回後の外観観察

[0028] a work example 2 -- [this work example] using the base material made from an aluminium of 50mmx100 mmx5mm thickness After performing a surface treatment as shown in Table 2, a size 20mmx20mmx5mm specimen is started from each base material, the mask of other portions is carried out so that the range whose surface treatment sides are 10mm x 10mm further may be exposed, and it glares on the following conditions for 20 hours. The amount of damages by plasma erosion was calculated as thinning thickness.
(1) Gas atmosphere and flow rate condition CF4, Ar, and the mixed gas of O2 were made into the atmosphere of the following conditions.
CF4/Ar/O2= 100/1000/10 ((flow rate cm3 per for 1 minute)2) Plasma irradiation output high frequency electric power : 1300 W pressure : 133.3 Pa [0029] The test result was shown in Table 2. Anodic oxide film according to the present technology of a comparative example so that clearly from the result shown in this table 2 (No.8) It begins and is B4C. Sprayed coating (No.10) It is imagined that is large and the amount of damages by plasma erosion is not all practical. However, it also sets to a comparative example. Al2O3 sprayed coating (No.9) Comparatively good plasma-proof erosion nature was shown. On the other hand, 2OY3 sprayed coating of this invention demonstrated the extremely excellent plasma-proof erosion nature, and maintaining good performance under the atmosphere containing a halogenated compound was accepted.
[0030]
[Table 2]

No.	溶射法	表面処理法	アンダーコートの有無	エロージョン損失深さ（μm）	備考
1	Y_2O_3 (99.9 %)	溶射	有	6.2	実施例
2			無	6.1	
3	Y_2O_3 (99.8 %)	溶射	有	7.6	
4			無	7.2	
5	Y_2O_3 (99.5 %)	溶射	有	6.5	
6			無	6.3	
7	Y_2O_3 (99.9 %)	PVD	無	6.6	比較例
8	Al_2O_3	陽極酸化	無	39.5	
9	Al_2O_3	溶射	有	8.1	
10	B_4C	溶射	有	28.0	
11	石英	—	無	39.0	

（備考）
(1) 溶射は大気プラズマ溶射法を用い、アンダーコートの膜厚80μm
Y_2O_3, Al_2O_3 などのトップコートの膜厚は 200μmに成膜
(2) アンダーコートの材質は80%Ni−20%Al
(3) 陽極酸化は JIS H8601規定のAA25に準じて成膜させたものである。

[0031] a work example 3 -- this work example -- the base material top made from an aluminium of 5mm of 50mm[in width] x length 100 mmx thickness -- as an under coat 80% nickel-20%aluminum -- as 80 micrometers and an intermediate layer Al2O3 -- or -- Al2O3 50vol%/Y2O3 50vol% of mixture 100 micrometers It is about Y2O3 on it. After forming membranes by air plasma spraying to 200-micrometer thickness, respectively, the plasma erosion examination was carried out on condition of the work example 2. As a result, the sprayed coating of this invention is an outermost layer part. (topcoat) As long as 2OY3 sprayed coating is formed, it is an intermediate layer. Even if it arranges Al2O3, Al2O3 / Y2O3 mixture layer, Influence is not received in plasma-proof erosion nature, but it is the exposure of 20 hours. 6.1-7.5 Elimination of mum did not pass to have accepted but demonstrating performance sufficient also with a multilayer structure coat was accepted.
[0032] a work example 4 -- the present in this work example base material made from an aluminium -- anodic oxidation (alumite treatment) Specimen carried out, It is the alloy film of 80%nickel-20%aluminum as an under coat on a base material. It covers to 100-micrometer thickness. It is 2OY3 coat as topcoat on it. 250 micrometers of specimens formed by plasma spraying, respectively are used. Plasma etching was performed on the following conditions and the particle number adhering to the surface of 8 inches in diameter the silicon wafer gently put into the same chamber compared the number of the particle grains which are deleted by etching and disperse. In addition, it investigates with surface inspection equipment and the adhering particle number is a grain size in general. It carried out for the grain of 0.2 micrometers or more.
(1) Gas atmosphere, flow rate condition CHF3, O2, and Ar were circulated by the respectively following mixing ratio.
CHF3/O2/Ar=80/100 /160 ((flow rate cm3 per for 1 minute)2) Plasma irradiation output high frequency electric power : 1300 W pressure : 4 Pa temperature : 60 ** [0033] It anodizes as a result of this experiment. (alumite film) In the specimen carried out, 30 of the particle management value 17.5 hours after plasma irradiation and in a general chamber are exceeded, and it is in 25 hours. It became 150 or more pieces. the presentation of this particle --

aluminum and F from -- it was what becoming. On the other hand, by 2OY3 sprayed coating which suits this invention, it became after the 70-hour exposure and the plasma-proof erosion nature which remained and was excellent in the grade exceeding a control limit value at last was shown.

[0034]

[Effect of the Invention] As explained above, according to this invention, it is 2OY3 sprayed coating on metallic or the nature base material of nonmetallic. By the member which formed directly, or constructed the metallic under coat upwards, and formed 2OY3 sprayed coating, when it is used under the environment where the plasma erosion operation under the gas atmosphere containing a halogenated compound is received, the outstanding resistance is shown. For this reason, even if it continues plasma etching work over a long time, it becomes the inside of a chamber has little contamination by a particle, and possible to produce quality products efficiently. Moreover, since the contamination velocity by the particle in a chamber becomes slow, the interval of defecation work becomes long, improvement in productivity can be expected, and it is very effective as inside material of a plasma treatment container.

[Translation done.]